

Two-dimensional polymer networks at a mixed boundary: Surface and wedge exponents

M. T. Batchelor¹, D. Bennett-Wood² and A. L. Owczarek²

¹ Department of Mathematics, School of Mathematical Sciences, The Australian National University, Canberra ACT 0200, Australia

² Department of Mathematics and Statistics, The University of Melbourne, Parkville, Victoria 3052, Australia

February 1, 2008

Abstract. We provide general formulae for the configurational exponents of an arbitrary polymer network connected to the surface of an arbitrary wedge of the two-dimensional plane, where the surface is allowed to assume a general mixture of boundary conditions on either side of the wedge. We report on a comprehensive study of a linear chain by exact enumeration, with various attachments of the walk's ends to the surface, in wedges of angles $\pi/2$ and π , with general mixed boundary conditions.

PACS. 05.70.Jk Critical point phenomena – 64.60.Cn Statistical mechanics of model systems – 61.41.+e Polymers

1 Introduction

The configurational properties of long self-avoiding polymer chains in the vicinity of a boundary has long been of interest [1]. Recent progress has involved combining general results from scaling and conformal invariance [2,3,4] with results from exactly solved lattice models. The canonical model of polymers in a solvent is that of self-avoiding walks (SAWs) on a lattice. A wall can be introduced by restricting the SAW to the upper half of the lattice, and the interaction with the surface by an energy, ϵ , associated with contacts between the polymer and the surface. The Boltzmann weight for a configuration of the polymer is given by $\kappa^m = e^{m\epsilon/k_B T}$, where T is the temperature of the solvent and m is the number of contacts with the surface. At some critical temperature, T_a , the polymer becomes adsorbed onto the surface [5]. For high temperatures, ($T > T_a$), the polymer is in a desorbed phase where it extends a large distance into the solvent above the surface to which it is attached. For low temperatures, ($T < T_a$), the polymer is in an adsorbed phase. It is well known [6] that there is a correspondence between SAWs and the $O(n)$ model in the limit $n \rightarrow 0$. The $O(n)$ model has been considered with three different boundary conditions: free boundary spins, where the bulk and surface couplings are the same; fixed boundary spins; and critically enhanced surface coupling [7]. In the terminology of surface critical phenomena these three boundary conditions correspond to the ‘ordinary’, ‘extraordinary’ and ‘special’ transitions. The critical adsorption temperature, T_a , for SAWs corresponds to the ‘special’ transition, whilst the ‘ordinary’ transition corresponds to SAWs in the presence of an effectively repulsive surface.

Recently Batchelor and Yung [8] derived the critical temperature and configurational exponent from the Bethe Ansatz solution of the $O(n)$ loop model with mixed boundary conditions on the honeycomb lattice. Here, ‘ordinary’ (o) boundary conditions apply to one side of the walk's origin, and ‘special’ (s) boundary conditions apply to the other. The general model with a flat surface and mixed boundary conditions on the honeycomb lattice has been discussed by Bennett-Wood and Owczarek [9] who verified the critical temperature and exponent values.

Here we provide the general formulae for the configurational exponents of an arbitrary polymer network connected to the surface of an arbitrary wedge of the two-dimensional plane where the surface is allowed to have general mixed boundary conditions. We also report on an extensive numerical study of this situation. This confirms the theory and brings together consistent numerics for all previously studied cases. Our results are given in Table 1.

2 Surface exponents for arbitrary mixed topology

We consider the most general mixed network of \mathcal{N} identical long self-avoiding polymer chains of lengths S . Each chain ends in a vertex. The surface geometry is depicted in Fig. 1. Vertices in the vicinity of the boundary where the boundary conditions change from o to s are denoted m. The topological characteristics are the numbers n_L of L -leg vertices in the bulk and n'_L of L -leg vertices near the surface. In particular, n'_L is the total number of vertices of each type, $n'_L = n_L^o + n_L^m + n_L^s$. In each case there can

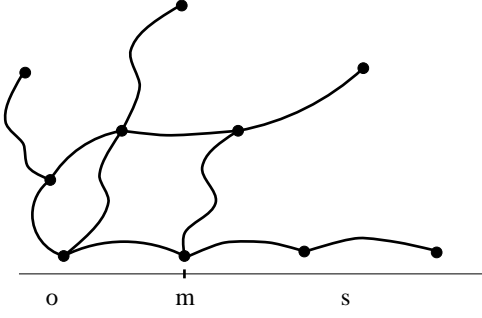


Fig. 1. A network made of $\mathcal{N} = 11$ chains at the mixed o-s boundary. There are $V = 6$ bulk vertices, with $n_1 = 3$, $n_3 = 2$, $n_4 = 1$ and $V' = 4$ surface vertices, with $n_3^o = 1$, $n_3^m = 1$, $n_1^s = 1$, $n_2^s = 1$.

be $L \geq 1$ vertices. The total number of bulk and surface vertices are given by $V = \sum n_L$ and $V' = \sum n'_L$. The number of chains can be written as $\mathcal{N} = \frac{1}{2} \sum (n_L + n'_L)L$.

The number of configurations \mathcal{Z}_G of the network is given by $\mathcal{Z}_G \sim \mu^{NS} S^{\gamma_G - 1}$ as $S \rightarrow \infty$. Here μ is the connective constant for SAWs. The general argument for the universal exponent γ_G follows that given in [10] for the polydisperse partition function, with result

$$\gamma_{G\text{poly}} = \nu \left[2V + V' - 1 - \sum_L (n_L x_L + n_L^o x_L^o + n_L^m x_L^m + n_L^s x_L^s) \right]. \quad (1)$$

We also make the assumption that the chains are monodisperse, with $\gamma_G = \gamma_{G\text{poly}} - \mathcal{N} + 1$. Collecting the terms, with $\nu = \frac{3}{4}$ [11], then gives

$$\begin{aligned} \gamma_G = \frac{1}{4} - \sum_L \left(\frac{3}{4} x_L + \frac{1}{2} L - \frac{3}{2} \right) n_L \\ - \sum_L \left(\frac{3}{4} x_L^o + \frac{1}{2} L - \frac{3}{4} \right) n_L^o \\ - \sum_L \left(\frac{3}{4} x_L^m + \frac{1}{2} L - \frac{3}{4} \right) n_L^m \\ - \sum_L \left(\frac{3}{4} x_L^s + \frac{1}{2} L - \frac{3}{4} \right) n_L^s, \end{aligned} \quad (2)$$

where the x_L are geometric scaling dimensions. These have all been derived for the bulk, ordinary, special and mixed transitions [12,13,14,8,15] from the exactly solved $O(n)$ model on the honeycomb lattice [16,13,17]. The dimensions x_L and x_L^o had been obtained earlier by conformal invariance and Coulomb gas methods [18,19,20,21,10]. In particular, at $n = 0$

$$\begin{aligned} x_L &= \frac{3}{16} L^2 - \frac{1}{12}, \\ x_L^o &= \frac{3}{8} L^2 + \frac{1}{4} L, \\ x_L^s &= \frac{3}{8} (L+1)^2 - \frac{3}{2} (L+1) + \frac{35}{24}, \\ x_L^m &= \frac{3}{8} L^2 - \frac{1}{4} L. \end{aligned} \quad (3)$$

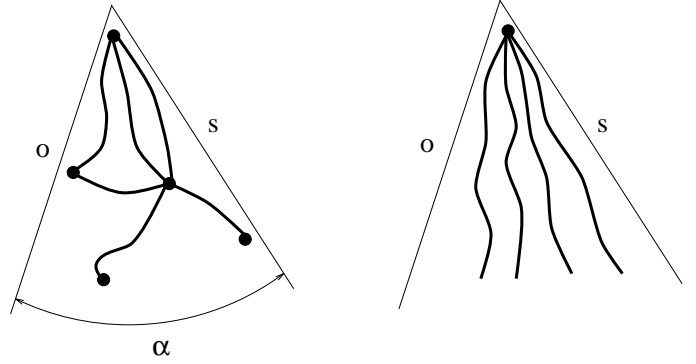


Fig. 2. (a) A mixed o-s network with a vertex in a wedge of angle α ; (b) a star polymer.

Inserting these results into (2) gives

$$\begin{aligned} \gamma_G = \frac{1}{4} + \frac{1}{64} \sum_L n_L (2-L)(9L+50) \\ - \frac{1}{32} \sum_L n_L^o (9L^2 + 22L - 24) \\ - \frac{1}{32} \sum_L n_L^m (9L^2 + 10L - 24) \\ - \frac{1}{32} \sum_L n_L^s (9L^2 - 2L - 16). \end{aligned} \quad (4)$$

The exponents for a pure ‘ordinary’ surface [10] are recovered with $n_L^m = n_L^s = 0$. For mixed boundaries there is only one L -leg vertex emanating from the origin, thus $n_L^m = 1$.

3 Wedge exponents

The network can be tied in a wedge of angle α by an \hat{L} -leg vertex as in Fig. 2. Obtaining the wedge network exponents $\gamma_G(\alpha)$ involves a conformal map of the wedge to the half-plane [21,10]. The final result

$$\gamma_G(\alpha) = \gamma_G(\pi) - \nu \left(\frac{\pi}{\alpha} - 1 \right) x'_L \quad (5)$$

is as given in [10], where now $\gamma_G(\pi)$ is the half-plane exponent (4). The contribution x'_L from the \hat{L} -leg tie depends on the particular surfaces under consideration, with $x'_L = x_L^m$ for the mixed boundary.

It follows from (4) and (5) that an L -leg star polymer confined to a wedge with o-o, s-s or o-s surfaces has exponents

$$\gamma_L^o(\alpha) = 1 + \frac{27L}{64} - \frac{3\pi L(3L+2)}{32\alpha}, \quad (6)$$

$$\gamma_L^s(\alpha) = 1 + \frac{27L}{64} - \frac{9\pi L(L-2) + 8\pi}{32\alpha}, \quad (7)$$

$$\gamma_L^m(\alpha) = 1 + \frac{27L}{64} - \frac{3\pi L(3L-2)}{32\alpha}. \quad (8)$$

The o-o result (6) is that obtained in [10]. As particular examples relevant to our numerical tests, consider a single SAW emanating from a 90° corner. In this case the above formulae reduce to $\gamma_1^o(\frac{\pi}{2}) = \frac{31}{64}$, $\gamma_1^s(\frac{\pi}{2}) = \frac{95}{64}$, $\gamma_1^m(\frac{\pi}{2}) = \frac{79}{64}$. The exponents differ if the walk terminates on either boundary. In that case (4) and (5) give $\gamma_{11}^o(\frac{\pi}{2}) = -\frac{21}{32}$ for the o-o corner and $\gamma_{11}^s(\frac{\pi}{2}) = \frac{27}{32}$ for the s-s corner. For the o-s corner the walk can terminate on either the o side, with $\gamma_{11}^{mo}(\frac{\pi}{2}) = \frac{3}{32}$, or on the s side, with $\gamma_{11}^{ms}(\frac{\pi}{2}) = \frac{19}{32}$.

4 Adsorption temperatures on the honeycomb lattice

There are two regular types of boundary of a honeycomb lattice. For the horizontal boundary of Fig. 3 the critical adsorption temperature is known to be given by [14]

$$\exp\left(\frac{\varepsilon}{kT_a}\right) = 1 + \sqrt{2} = 2.414 \dots \quad (9)$$

This result follows from the boundary vertex weights of the corresponding exactly solvable $O(n)$ loop model [17].

The adsorption temperature for the vertical boundary of Fig. 3 can be determined in a similar way. Specifically, the horizontal boundary in Fig. 3 follows on taking the value $u = \lambda$ in the vertex weights of the more general solvable loop model on the square lattice [14]. The vertical boundary in Fig. 3 follows on taking the value $u = 2\lambda$. As a result the critical fugacity of a step along the boundary is given by $y^* = 1/\sqrt{t_b t_s}$ where $t_b = 2 \cos \frac{\pi}{8} = (2 + \sqrt{2})^{1/2}$ and $t_s^2 = \cos \frac{5\pi}{16} / \cos \frac{\pi}{16} = t_b^2 - t_b - 1$. The critical adsorption temperature is thus given by

$$\exp\left(\frac{\varepsilon}{kT_a}\right) = \sqrt{\frac{2 + \sqrt{2}}{1 + \sqrt{2} - \sqrt{2 + \sqrt{2}}}} = 2.455 \dots \quad (10)$$

5 Results from exact enumeration

The general theory presented above generalises that already given for polymer networks in wedges of arbitrary angles [10] to the case of mixed boundary conditions. To test the exponent predictions in this case we have enumerated SAWs on the honeycomb lattice with various ends attached to a surface and confined in wedges of two different angles ($\pi/2$ and π). This also allows us to verify the critical boundary temperature (10). The critical temperature (9) and the exponent $\gamma_1^m(\pi)$ have been verified previously [9]. (A comprehensive account of this study can be found in [22].) Previous numerical work other than [9] has focused on the square and triangular lattices. However, our numerical task is made considerably easier since the exact prediction for the connective constant for SAWs on the honeycomb lattice, $\mu = \sqrt{2 + \sqrt{2}}$, allows the biasing of exponent estimates.

In this letter we consider two particular situations: SAWs restricted to the upper half plane of the honeycomb

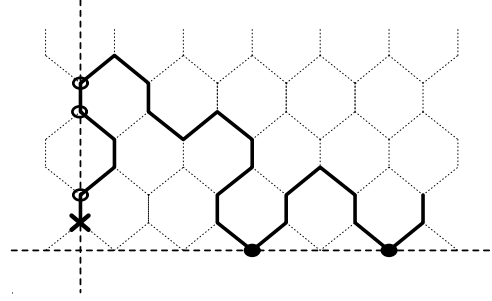


Fig. 3. A SAW (origin denoted by a cross) on the honeycomb lattice attached to the vertex of a 90° wedge with contacts identified with the vertical boundary (open circles) and with the horizontal boundary (closed circles). A fugacity κ_v is associated with open circle contacts while a fugacity κ_h is associated with closed circle contacts. (The walk is not permitted to go beyond the indicated dotted lines.)

lattice with fugacities κ_l and κ_r associated with contacts between the walk and either side of the surface as shown in Fig. 1 of [9], and more importantly SAWs restricted to the positive quadrant of the honeycomb lattice, where the fugacities κ_v and κ_h are associated with contacts between the walk and the vertical and horizontal surfaces, respectively, as shown in Fig. 3. The partition function for walks of length n with one end attached to a surface, with different energies for sites interacting with either side of a $\pi/2$ wedge (see Fig. 3), is given by

$$Z_n^1(\kappa_v, \kappa_h, \pi/2) = \sum_{m_v, m_h} c_n^1(m_v, m_h, \pi/2) \kappa_v^{m_v} \kappa_h^{m_h}, \quad (11)$$

where the sum is over all allowed values of the number of contacts m_v with the vertical boundary, and the number of contacts m_h with the horizontal boundary. The coefficients $c_n^1(m_v, m_h, \pi/2)$ are the number of configurations of length n with m_v and m_h vertical and horizontal interactions respectively. The partition functions for walks with the both ends attached, $Z_n^{11}(\kappa_v, \kappa_h, \pi/2)$, simply replaces $c_n^1(m_v, m_h, \pi/2)$ with $c_n^{11}(m_v, m_h, \pi/2)$ for configurations attached at both ends. Also, in the cases, as described in [9], associated with a flat surface (wedge angle π), the partition functions, $Z_n^1(\kappa_l, \kappa_r, \pi)$ and $Z_n^{11}(\kappa_l, \kappa_r, \pi)$, are defined with the obvious modifications. Tables of the various coefficients $c_n^1(m_v, m_h, \pi/2)$, etc. can be found in [22]¹. Cases where walks traverse from one side of the wedge to the other have also been considered but numerical difficulties hampered exponent calculation and hence we do not present those results here [22]. The method of enumeration of the coefficients was via a backtracking algorithm, which was implemented (on a small supercomputer) in a similar way to that described in [9].

By setting the interaction parameters to the particular values, e.g. those implied from the critical temperature values given in the previous section, estimates of the various exponents were obtained by analysis of the singularity structure of generating functions of the resulting partition

¹ or via email to aleks@ms.unimelb.edu.au

Table 1. Our estimates for the entropic exponent γ for SAWs attached to a flat surface or $\pi/2$ wedge.

numerical	predicted
$\gamma_1^o(\pi) = 0.9531(5)$	$(\frac{61}{64} = 0.953125)$
$\gamma_{11}^o(\pi) = -0.186(2)$	$(-\frac{3}{16} = -0.1875)$
$\gamma_1^o(\pi/2) = 0.4843(9)$	$(\frac{31}{64} = 0.484375)$
$\gamma_{11}^o(\pi/2) = -0.655(3)$	$(-\frac{21}{32} = -0.65625)$
$\gamma_1^s(\pi) = 1.451(2)$	$(\frac{93}{64} = 1.453125)$
$\gamma_{11}^s(\pi) = 0.813(4)$	$(\frac{13}{16} = 0.8125)$
$\gamma_1^s(\pi/2) = 1.482(8)$	$(\frac{95}{64} = 1.484375)$
$\gamma_{11}^s(\pi/2) = 0.85(1)$	$(\frac{27}{32} = 0.84375)$
$\gamma_1^m(\pi) = 1.3279(5)$	$(\frac{85}{64} = 1.328125)$
$\gamma_{11}^{mo}(\pi) = 0.183(6)$	$(\frac{3}{16} = 0.1875)$
$\gamma_{11}^{ms}(\pi) = 0.689(9)$	$(\frac{11}{16} = 0.6875)$
$\gamma_1^m(\pi/2) = 1.233(6)$	$(\frac{79}{64} = 1.234375)$
$\gamma_{11}^{mo}(\pi/2) = 0.09(1)$	$(\frac{3}{32} = 0.09375)$
$\gamma_{11}^{ms}(\pi/2) = 0.596(7)$	$(\frac{19}{32} = 0.59375)$

functions. The method of analysis was based primarily on biased differential approximants as explained in [9].

For completeness we give estimates of all the exponents $\gamma_1(\pi)$ and $\gamma_{11}(\pi)$, and $\gamma_1(\pi/2)$ and $\gamma_{11}(\pi/2)$ for each boundary condition. In most cases the numerical accuracy equals or surpasses previous estimates. It should be noted though that errors quoted are *not* rigorous bounds and represent the spread of the approximants' exponent values (at the critical point). The difference in the accuracy (some values are more accurate, e.g. $\gamma_1^o(\pi)$, than the errors — which are conservative — suggest) can be argued to be due to the amount of shift required in biasing the approximants, which is itself an indication of the relative convergence of the series to the asymptotic forms expected. A full discussion of how the errors and final estimates were obtained can be found in [22], following the general lines given in [9]. Our estimates for all exponents are in good agreement with the predicted values and are given in Table 1. The verification of the special exponents involved the implicit verification of the vertical adsorption temperature, eqn. (10).

6 Conclusion

We present the general results for the entropic exponents of a polymer network in two dimensions attached to the surface in a general wedge topology. We have verified that the theoretical formulae, coming from a combination of scaling and conformal invariance considerations and exact results, are correct by extensively analysing exact enumeration data from SAWs on the honeycomb lattice. Where numerical evidence has been precise confirmation of the theory has been good. However, several questions remain. One is the numerical confirmation of exponents in this general setting for more complicated examples. Another

associated question is the validity of one of the assumptions of the theory concerning polydisperse versus monodisperse cases [23]. Such studies are outside the range of current exact enumeration and probably require careful Monte Carlo work.

Acknowledgments

It is a pleasure to thank John Cardy for explaining the general scaling and conformal invariance arguments to us. Two of us (MTB and ALO) have been supported by the Australian Research Council.

References

1. M. N. Barber, A. J. Guttmann, K. M. Middlemiss, G. M. Torrie and S. G. Whittington, J. Phys. A **11**, (1978) 1833.
2. K. De'Bell and T. Lookman, Rev. Mod. Phys. **65**, (1993) 87.
3. E. Eisenriegler, Polymers Near Surfaces (World Scientific, Singapore, 1993).
4. J. Cardy, Scaling and Renormalization in Statistical Physics (CUP, Cambridge, 1996).
5. J. M. Hammersley, G. M. Torrie and S. G. Whittington, J. Phys. A **15**, (1982) 539.
6. P. G. de Gennes, Scaling concepts in polymer physics (Cornell University, 1979).
7. T. W. Burkhardt and E. Eisenriegler, Nucl. Phys. B **424**, (1994) 487.
8. M. T. Batchelor and C. M. Yung, J. Phys. A **28**, (1995) L421.
9. D. Bennett-Wood and A. L. Owczarek, J. Phys. A **29**, (1996) 4755.
10. B. Duplantier and H. Saleur, Phys. Rev. Lett. **57**, (1986) 3179; B. Duplantier, J. Stat. Phys. **54**, (1989) 581.
11. B. Nienhuis, Phys. Rev. Lett. **49**, (1982) 1062.
12. M. T. Batchelor and H. W. J. Blöte, Phys. Rev. B **39**, (1989) 2391.
13. M. T. Batchelor and J. Suzuki, J. Phys. A **26**, (1993) L729.
14. M. T. Batchelor and C. M. Yung, Phys. Rev. Lett. **74**, (1995) 2026.
15. C. M. Yung and M. T. Batchelor, Nucl. Phys. B **453**, (1995) 552.
16. R. J. Baxter, J. Phys. A **19**, (1986) 2821.
17. C. M. Yung and M. T. Batchelor, Nucl. Phys. B **435**, (1995) 430.
18. B. Nienhuis, J. Stat. Phys. **34**, (1984) 731.
19. H. Saleur, J. Phys. A **20**, (1987) 455; **19**, (1986) L807.
20. B. Duplantier, Phys. Rev. Lett. **57**, (1986) 941.
21. J. L. Cardy, Nucl. Phys. B **240**, (1984) 514.
22. D. Bennett-Wood, Ph. D. Thesis, University of Melbourne (1998).
23. At some length this is discussed in L. Schäfer, C. von Ferber, U. Lehr and B. Duplantier, Nucl. Phys. B **374**, (1992) 473.